Table I. Product Yields from the Decomposition of **1** in the Presence of CO and Added Gases

Reactant(s)	N_2, mmol	Product[a] C_3O_2, mmol × 10^2	Other products,[b] mmol × 10^3
200 mm of CO	0.91 ± 0.02	1.2 ± 0.1	
200 mm of CO + 5% O_2		1.0 ± 0.1	
200 mm of CO + 10% O_2		1.2	
200 mm of CO + 20% O_2		1.1	
200 mm of CO + 100 mm of Ar		1.0	
200 mm of CO + 200 mm of Ar		1.1	
200 mm of CO + 350 mm of Ar		1.0	
200 mm of CO + 200 mm of CH_4		1.0 ± 0.1	$CH_2{=}C{=}O$, 0.23 ± 0.04; C_2H_4, 7.5 ± 0.5; C_2H_6, 0.2
200 mm of CH_4			C_2H_4, 4.7 ± 0.5
200 mm of CO + 200 mm of C_2H_4		<0.7[c]	$CH_2{=}C{=}CH_2$, 2.5; $CH_3C{\equiv}CH$, 2.0

[a] All products were identified by their ir spectra with the exception of ethane and propyne which were identified by gc retention times. [b] In all experiments HCN and C_2H_2 are produced. These products have not been included as they do not result from the reaction of carbon atoms with CO. [c] C_3O_2 was not detected by ir; a gc analysis was not performed.

In order to determine the spin state of the reacting carbon atom in our system, we have carried out the pyrolysis of **1** in the presence of carbon monoxide and various added gases. The results of these studies are given in Table I. The yield of carbon suboxide reported for the decomposition of **1** in the presence of 200 mm of carbon monoxide is an average of nine runs which have a standard deviation of 7 × 10^{-4} mmol. Assuming that 3 mol of nitrogen is produced per mol of carbon atom, the yield of carbon suboxide from atomic carbon is 4%. However, this is a lower limit for the yield of carbon suboxide since nitrogen may also be produced in processes which do not result in the formation of carbon atoms.

The results in Table I show that added oxygen has little effect on the yield of carbon suboxide. Since oxygen is known to be an effective scavanger of $C(^3P)$,[2,5,9] we conclude that ground-state carbon atoms are not extensively involved in the production of carbon suboxide. Triplet carbon atoms may be produced in the decomposition of **1**, but they do not react appreciably to give carbon suboxide. An attempt was made to degrade the reacting carbon atoms to their triplet ground state with increasing pressure of added argon. Table I shows that added argon has little effect on the yield of carbon suboxide. This is not surprising as flash photolysis studies[10] have shown that the rate of collisional deactivation of $C(^1D)$ to ground state by argon is small compared to the rates of reaction of $C(^1D)$.

Decomposition of **1** in an atmosphere of carbon monoxide and methane (Table I) yields ethylene as one of the products. This result is consistent with the formation of C_2O. Ethylene is known to result from the reaction of C_2O and methane.[11] Ethylene may also arise by direct reaction of carbon atoms with methane. The data in Table I show that this reaction does take place, but that the yield of ethylene is greater in the presence of a mixture of carbon monoxide and methane than in methane alone. In the reaction of carbon atoms with carbon monoxide and methane, small amounts of ketene are also produced. Possible mechanisms for the formation of ketene include (1) reaction of methylene (formed by hydrogen abstraction) with carbon monoxide or (2) hydrogen abstraction by C_2O. The formation of ketene by the reaction of methylene with carbon monoxide has been reported.[12] It is also of interest that radiolysis of carbon monoxide in the presence of methane results in the formation of ketene.[13]

The reaction of C_2O with ethylene is known to produce allene and propyne.[14] The table shows that these two substances are formed when **1** is decomposed in an atmosphere of carbon monoxide and ethylene. This result is complicated by the fact that allene and propyne are also formed by direct reaction of carbon with ethylene.[1-3] However, the yields of propyne and allene are lower when there is no carbon monoxide present. Hence, the C_2O formed appears to be trapped by ethylene.

These data provide further evidence that atomic carbon is produced in the thermal decomposition of **1**. The results of experiments carried out in the presence of oxygen indicate that products arise from the reaction of singlet carbon. A continuing problem is the low yields of products in these reactions. We are trying to circumvent this difficulty by isolation of the parent diazo compound followed by gas-phase photolysis or thermolysis.

Acknowledgment. We thank the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research.

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(9) F. Martinotti, M. J. Welch, and A. P. Wolf, *Chem. Commun.*, 115 (1968).

(10) D. Husain and L. J. Kirsh, *Trans. Faraday Soc.*, **67**, 2886 (1971).

(11) K. Bayes, *J. Amer. Chem. Soc.*, **83**, 3712 (1961); E. Tschuikow-Roux, Y. Inel, S. Kodama, and A. W. Kirk, *J. Chem. Phys.*, **56**, 3288 (1972).

(12) T. B. Wilson and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, **80**, 2934 (1968).

(13) H. W. Buschmann and W. Groth, *Z. Naturforsch. A*, **22**, 954 (1967).

(14) D. G. Williamson and K. D. Bayes, *J. Amer. Chem. Soc.*, **90**, 1957 (1968).

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Reaction of Allylic Thioethers with Elemental Sulfur[1]

Sir:

Dialkyl sulfides, such as diethyl and dibenzyl sulfide, appear to be completely inert toward sulfurization with S_8 in Me_2SO-d_6, even when heated at *ca.* 80–90°

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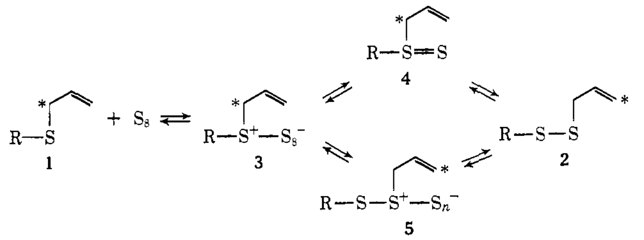
for several days.[2] By contrast, under the same conditions allyl methyl sulfide (**1a**) and diallyl sulfide (**1b**) are partially (*ca.* 40%) converted to the corresponding disulfides **2a** and **2b**.[4] The 40% conversion factor represents an approximate equilibrium distribution[5] since solutions of **2a** and **2b**, in the absence of S_8, undergo spontaneous thermal desulfurization[6] to yield mixtures in which the equilibrium ratios **1a**:**2a** and **1b**:**2b** are closely similar to those obtained by the direct sulfurization of the monosulfides; hence, the reaction is reversible. Furthermore, sulfurization of **1a** (and presumably **1b**) occurs with complete (by nmr) allylic rearrangement, as demonstrated by the conversion of allyl-*1,1*-d_2 methyl sulfide to allyl-*3,3*-d_2 methyl disulfide.[8,11]

We believe that these observations may be most succinctly accommodated by a scheme in which **1** and **2** are connected through a series of equilibria involving the intermediacy of dipolar polysulfide chains (**3**). Scheme I represents a small portion of a presumably complex network of interconversions. Thus, it depicts only the principal reaction pathways leading to disulfide **2**, with no attempt being made to explicitly account for the variety of reactions which may be implicated in the formation of polysulfides.

Scheme I[a,b]



[a] **a**, R = CH_3; **b**, R = $CH_2CH{=}CH_2$. The asterisk denotes a label. [b] For simplicity, no attempt has been made to represent stoichiometry in this scheme. Thus, for example, *n* = 7 for **3** → **5** and *n* = 8 for **2** → **5**.

It is reasonable to assume that the first step in the postulated reaction scheme (**1** → **3**) involves heterolysis of a sulfur–sulfur bond in S_8 brought about by nucleophilic attack of the sulfur atom in **1**. Mechanistically, this opening of the S_8 ring is completely analogous to the initial step in the nucleophilic degradation of sulfur by triphenylphosphine[13] and other reagents.[14,15] For nucleophiles such as phosphines, degradation of the first-formed intermediate (*i.e.*, the phosphonium octasulfide analog of **3**)[13] is essentially irreversible, the driving force deriving from the stability of the ultimate product, the phosphine sulfide. In contrast, thiosulfoxides (**4**), which might be expected to form in a manner analogous to the phosphine sulfides, are unstable species whose inferred existence has never been confirmed by isolation.[16] However, whereas no observable reaction takes place between nonallylic thioethers and elemental sulfur, the presence of an allyl group completely changes the picture: energetically favorable pathways become available which are capable of leading to stable products. It has recently been demonstrated that allylic disulfides undergo unusually facile thermal rearrangements.[7,17] These reactions have been rationalized by postulating an equilibrium, by way of intramolecular [2,3] sigmatropic shifts, between allylic disulfides and the corresponding thiosulfoxides, the latter presumably existing in concentrations too minute to be readily detectable by direct observation.[18,19] Accordingly, it may be postulated that thiosulfoxides (**4**) are indeed formed under the conditions of sulfurization but they are largely diverted into the more stable linear disulfides (**2**), and that the equilibrium is thus displaced toward reaction product. The [2,3] sigmatropic rearrangement thus functions as a mechanism for trapping sulfur in these allylic systems. In a more speculative vein, one might imagine that a [2,3] sigmatropic shift along the linear polysulfide chain (**3** → **5**), followed by cleavage, yields **2** directly, *i.e.*, without intervention of **4**. Our data cannot exclude this as a possible alternate pathway.

In addition, there appear to exist pathways for the direct transfer of sulfur from disulfides to monosulfides. Thus **2a**, in the absence of S_8, serves as a sulfurizing reagent toward **1b**; similarly, **2b** is able to effect the sulfurization of **1a**. The reversible nature of these sulfurization and desulfurization processes is strikingly emphasized by the observation that in each of these sulfur transfer reactions, disulfide/sulfide product ratios result which are nearly identical for the diallyl and

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(2) It has been reported that at temperatures below about 170°, there is no observable reaction of dimethyl sulfide with sulfur over a period of several months.[3]

(3) D. Grant and J. R. Van Wazer, *J. Amer. Chem. Soc.*, **86**, 3012 (1964).

(4) The reactions are conveniently monitored by ^1H nmr (Me_2SO-d_6) and glpc (5% Carbowax 20M on Chromosorb W, 45–145°) analysis. The nmr signals in **1a** arising from the methyl and α-methylene protons are shifted downfield by *ca.* 0.40 and 0.28 ppm, respectively, upon conversion to **2a**; similar spectral shifts are exhibited by **1b**/**2b**.

(5) A true state of equilibrium is not attained since prolonged reaction leads to the formation and steady accumulation of tri-, tetra-, and higher polysulfides, identified on the basis of the nmr spectra.

(6) The spontaneous loss of sulfur from **2a** has been noted previously.[7]

(7) G. Höfle and J. E. Baldwin, *J. Amer. Chem. Soc.*, **93**, 6307 (1971).

(8) The deuterated sulfide was obtained *ca.* 98% isotopically pure by the reaction of allyl-*1,1*-d_2 bromide with sodium methylmercaptide in pentane; the bromide was obtained by the reaction of allyl-*1,1*-d_2 alcohol[9] with carbon tetrabromide and tri-*n*-octylphosphine.[10]

(9) R. D. Schuetz and F. W. Millard, *J. Org. Chem.*, **24**, 297 (1959).

(10) J. Hooz and S. S. H. Gilani, *Can. J. Chem.*, **46**, 86 (1968).

(11) A control experiment showed that the extent of thioallylic rearrangement[12] is negligible under the conditions of the sulfurization reaction.

(12) H. Kwart and N. Johnson, *J. Amer. Chem. Soc.*, **92**, 6064 (1970).

(13) P. D. Bartlett and G. Meguerian, *J. Amer. Chem. Soc.*, **78**, 3710 (1956).

(14) H. Schumann in "Sulfur in Organic and Inorganic Chemistry," Vol. 3, A. Senning, Ed., Marcel Dekker, New York, N. Y., 1972, Chapter 21.

(15) Sulfur-saturated Me_2SO solutions of **1** exhibited reaction rates roughly tenfold greater than those observed with less polar solvents such as methylcyclohexane. The solvent effect is thus much less pronounced than that observed in the sulfurization of phosphines.[13]

(16) Structures containing sulfur–sulfur double bonds are known in compounds other than thiosulfoxides, *e.g.*, difluoro disulfide (R. L. Kuczkowski, *J. Amer. Chem. Soc.*, **86**, 3617 (1964); F. Seel, R. Budenz, and D. Werner, *Chem. Ber.*, **97**, 1369 (1964)) and thiono sulfites (Q. E. Thompson, M. M. Crutchfield, and M. W. Dietrich, *J. Org. Chem.*, 30, 2696 (1965)).

(17) D. Barnard, T. H. Houseman, M. Porter, and B. K. Tidd, *Chem. Commun.*, 371 (1969); B. K. Tidd, *Int. J. Sulfur Chem. C*, **6**, 101 (1971).

(18) For a recently reported extension of these reactions to selenium systems, see K. B. Sharpless and R. F. Lauer, *J. Org. Chem.*, **37**, 3973 (1972).

(19) Allylic [2,3] sigmatropic shifts also interconvert linear and branched isomers in the closely analogous allyl sulfenate–allyl sulfoxide[20] and allyl thiophosphinite–allylphosphine sulfide[21] systems. However, in these systems the branched isomers are, in general, the thermodynamically more stable ones.

(20) R. Tang and K. Mislow, *J. Amer. Chem. Soc.*, **92**, 2100 (1970), and references cited therein.

(21) W. B. Farnham, A. W. Herriott, and K. Mislow, *J. Amer. Chem. Soc.*, **91**, 6878 (1969), and references cited therein.

allyl methyl systems, regardless of either the initial reactant ratio or the identity of the system originating as disulfide. Moreover, when an excess of disulfide is employed, higher disulfide/sulfide ratios are obtained for the system originating as the monosulfide than are possible from direct sulfurization with elemental sulfur, suggesting that S_8 is not an intermediate in the sulfur transfer reaction.

The above considerations suggest that nonallylic thioethers such as diethyl sulfide also react with elemental sulfur to a slight extent, and that the corresponding thiosulfoxides may thus be directly accessible, albeit in low concentrations.

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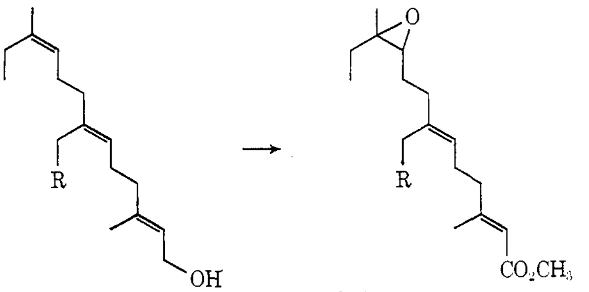
New Thiane Chemistry. The Conceptually Simple and Technically Practical Total Synthesis of *Cecropia* Juvenile Hormones

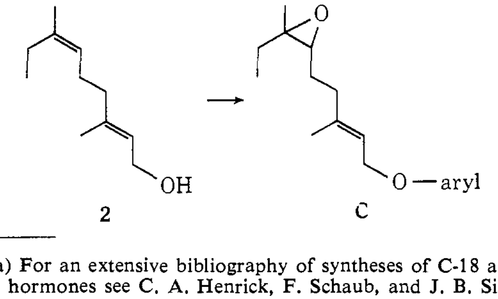
Sir:

In the last several years, much attention has been directed toward the chemistry and synthesis of *Cecropia* juvenile hormones A and B and related physiologically active analogs C. Many of the reported syntheses[1] of A and B describe ingeniously new general approaches to the stereoselective formation of unsymmetrically trisubstituted olefins, but these methods have often involved sequences too long and complicated for efficient construction of the structurally simple, acyclic terpenoids A and B. When the structural requirements of an effective synthesis were simplified even further by Corey's demnstration[1b] that farnesol homologs **1** are excellent precursors to A and B, we became convinced that a simple and effective total synthesis of the juvenile hormones should be demonstrable using a synthetic design specifically tailored to the preparation of trienols **1**. We now wish to report our observations that one such synthetic design makes possible, from *readily available* materials, the short, practical, and high-yield total synthesis of alcohols **1** and **2** and, consequently, of C_{18} and C_{17} *Cecropia* juvenile hormones and a number of active analogs.



1a, R = CH_3
1b, R = H

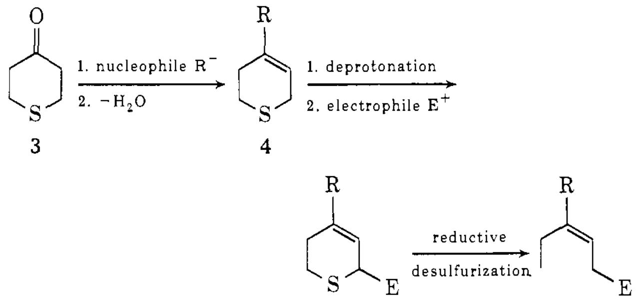
A, R = CH_3
C_{18} *Cecropia* juvenile hormone
B, R = H
C_{17} *Cecropia* juvenile hormone



2

C

We chose to rely on a classically well-known method for fixing the geometry of acyclic olefins, that of forming the olefin as part of a ring and subsequently cleaving the ring; we also anticipated using a modification of Biellmann's elegant allylic coupling,[2,2c] involving the alkylation of allyl sulfide carbanions, for assembling the carbon skeleton. As the logical consequence of combining these two synthetic methods, we were led to an approach which would utilize the same sulfur functionality as a ring bridging member (thus allowing predictable double bond geometry) and as a carbanion stabilizing group (thus allowing new carbon–carbon bond formations at predictable sites).[3] Consequently, the readily available and symmetrical 4-thiacyclohexanone **3**[4] served as the precursor to olefin units having a cis ethyl substituent, as represented below.



In 90% yield, **3** was converted to the known 4-thia-1-methylcyclohexene-1 (**4a**) (R = CH_3)[5] (methylmagnesium chloride in ether followed by dehydration with $POCl_3$ in pyridine–benzene). Ketone **3** was also converted in greater than 75% yield to the crystalline epoxide **5**, mp 49–50°,[6] using dimethylsulfoxonium methylide[7] (in Me_2SO at room temperature[7b] for 3 hr);

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[1] (a) For an extensive bibliography of syntheses of C-18 and C-17 juvenile hormones see C. A. Henrick, F. Schaub, and J. B. Siddall, *J. Amer. Chem. Soc.*, **94**, 5374 (1972); R. T. Anderson, C. A. Henrick, J. B. Siddall, and R. Zurfluh, *ibid.*, **94**, 5379 (1972); (b) E. J. Corey, J. A. Katzenellenbogen, N. W. Gilman, S. A. Roman, and B. W. Erickson, *J. Amer. Chem. Soc.*, 90, 5618 (1968); E. J. Corey and H. Yamamoto, *J. Amer. Chem. Soc.*, **92**, 6636 (1970).

[2] (a) J. F. Biellmann and J. B. Ducep, *Tetrahedron Lett.*, 5629 (1968); 3707 (1969); *Tetrahedron*, **27**, 5861 (1971). (b) A Biellmann coupling was used in the final steps of a recent synthesis of **1a** by E. E. van Tamelen, P. McCurry, and N. Huber, *Proc. Nat. Acad. Sci. U. S.*, **68**, 1294 (1971).

(2c) NOTE ADDED IN PROOF. A synthetic approach similar to the one we now report has also been described recently by K. Kondo, A. Negishi, K. Matsui, D. Tunemoto, and S. Masamune, *J. Chem. Soc., Chem. Commun.*, 1311 (1972).

[3] A preliminary report of this research was made by the principal investigator at the 164th National Meeting of the American Chemical Society, New York, N. Y., Aug 1972, Abstract ORGN-75.

[4] Ketone **3** is derived *via* Dieckmann condensation of dimethyl thiodipropionate (from the commercially available diacid or by bis addition of methyl acrylate to hydrogen sulfide). Reproducibly satisfactory yields of **3** were obtained as reported by E. A. Fehnel and M. Cormack, *J. Amer. Chem. Soc.*, **70**, 1813 (1948).

[5] (a) A modification of the procedure reported by R. F. Naylor, *J. Chem. Soc.*, 2749 (1949). (b) The endocyclic olefin **4a** is contaminated by about 7% exocyclic isomer. This contaminant is inert during the generation and alkylation of the carbanion **6** and is sufficiently volatile to allow easy separation from alkylation products of **4a**.

[6] Satisfactory spectral and physical properties were observed for all new compounds; high-resolution mass spectrometric analyses confirm all structural assignments; satisfactory combustion analyses further confirm structural assignments of crystalline compounds.

[7] (a) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1353 (1965). (b) The procedure employed is a modification of ref 7a. Reaction at room temperature was necessary for satisfactory transformation